

Data collection

Stoe–Siemens AED diffractometer
 $\omega/2\theta$ scans with profile fitting (Clegg, 1981)
 Absorption correction: none
 2171 measured reflections
 2131 independent reflections
 1241 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 25^\circ$
 $h = -11 \rightarrow 2$
 $k = 0 \rightarrow 14$
 $l = 0 \rightarrow 16$
 3 standard reflections every 200 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.117$
 $S = 1.005$
 2131 reflections
 209 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.13 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.13 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.013 (2)
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

N1—C2	1.249 (5)	N4—C5	1.263 (4)
N1—C6	1.453 (5)	C5—O51	1.346 (4)
C2—O21	1.353 (4)	C5—C6	1.496 (5)
C2—C3	1.498 (5)	O7—N8	1.412 (3)
C3—N4	1.436 (4)	N8—C9	1.267 (4)
C3—O7	1.465 (4)	C9—C10	1.500 (4)
C3—C10	1.523 (4)		
C2—N1—C6	118.1 (4)	N1—C6—C5	113.6 (3)
N1—C2—C3	127.6 (4)	N8—O7—C3	109.4 (2)
N4—C3—C2	114.5 (3)	C9—N8—O7	109.8 (3)
O7—C3—C10	104.1 (3)	N8—C9—C10	114.1 (4)
C5—N4—C3	117.6 (3)	C9—C10—C3	101.5 (3)
N4—C5—C6	128.0 (4)		

The absolute configuration of the title compound could not be determined experimentally, but was established from the known configuration at C6 (*S*). All H atoms were located by a difference Fourier synthesis and refined with fixed individual displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ or $1.2U_{\text{eq}}(\text{C})$], using a riding model with C—H(aromatic) = 0.93, C—H(tertiary) = 0.98, C—H(secondary) = 0.97 or C—H(methyl) = 0.96 \AA . Atom C63 shows slightly high anisotropic displacement parameters, but there is no disorder present and the C61—C63 bond is of normal length.

Data collection: *DIF4* (Stoe & Cie, 1984a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1984b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1299). Services for accessing these data are described at the back of the journal.

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1-(2,4-Dinitrophenyl)-3-(2-hydroxyphenyl)-1*H*-pyrazole-4-carbaldehyde

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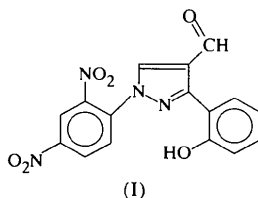
Abstract

In the crystal of the title compound, $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_6$, the dinitrophenyl and hydroxyphenyl groups are oriented at angles of 43.8(1) and 28.0(1) $^\circ$, respectively, with respect to the pyrazole ring. The internal C—C—C ring angles at the *o*- and *p*- positions, where NO_2 is bonded, are 121.6(2) and 122.3(2) $^\circ$. The crystal structure and packing are stabilized by O—H \cdots N and C—H \cdots O hydrogen bonds.

Comment

Pyrazole and several of its N-substituted derivatives are used as inhibitors and deactivators of liver alcohol dehydrogenase and many pyrazole derivatives have pharmaceutical applications such as analgesic, antipyretic and anti-inflammatory effects (Potts, 1996). Pyrazole

derivatives have also been found to possess moderate antimalarial activity (Garg *et al.*, 1973) and they have many important applications in the areas of medicine, agriculture, and also synthetic organic chemistry (Weily & Wiley, 1964; Taki *et al.*, 1992). In view of the wide biological applications of pyrazole compounds, the crystal structure of 1-(2,4-dinitrophenyl)-3-(2-hydroxyphenyl)-1*H*-pyrazole-4-carbaldehyde, (I), has been determined.



Bond lengths and bond angles in the pyrazole ring are comparable with the reported values of similar pyrazole structures (Bonati & Bovio, 1990; Fronczek *et al.*, 1989; Mani Naidu *et al.*, 1996; Malhotra *et al.*, 1997). The widening of the exterior angles at the substituted C and N atoms are also observed. The sums of the bond angles around the N2, N3 and N4 atoms are 359.2 (2), 360.0 (2) and 360.1 (2)°, respectively, which indicates the *sp*² hybridization. The C_{sp}—OH [1.368 (3) Å] and C*sp*²=O distances [1.206 (3) Å] compare well with the average values of 1.362 and 1.192 Å, respectively, reported in the Cambridge Structural Database (Allen *et al.*, 1987).

In the phenyl ring, the internal ring angles at the C atoms to which the NO₂ are bonded in the *o*- [121.6 (2)°] and *p*- [122.3 (2)°] positions are in agreement with the values from molecular orbital calculations [122.3°] and for nitrobenzene [122.7 (1)°] in a crystalline environment (Domenicano *et al.*, 1990). Also, the absence of π - π stacking interactions indicates that the electronic interaction of the nitro group with the ring occurs primarily at the σ level, with limited transfer of π electrons from the ring to the substituent.

The hydroxyphenyl and dinitrophenyl rings are planar with maximum deviations of -0.013 (2) and -0.030 (2) Å, respectively, for the atoms connected to the pyrazole ring. Ellena *et al.* (1996) have reported a slightly deformed boat conformation for the dinitrophenyl ring in 2,4-dinitrophenyl phenyl sulfone where the total puckering amplitude Q_T is 0.028 (4) Å and the *o*-NO₂ is rotated 56.5 (2)° out of the ring plane and *p*-NO₂ is twisted out of plane by 18.5 (3)°. The carbaldehyde group in (I) is twisted by 6.4 (2)° from the best plane of the pyrazole ring and is in synperiplanar orientation with the ring as can be seen from the torsion angle C7—C8—C10—O2 [-7.4 (3)°]. The C*sp*²—N bonds associated with the nitro groups are clearly single bonds, while the N1—C7 [1.343 (2) Å] bond shows partial double-bond character (Mani Naidu *et al.*, 1996).

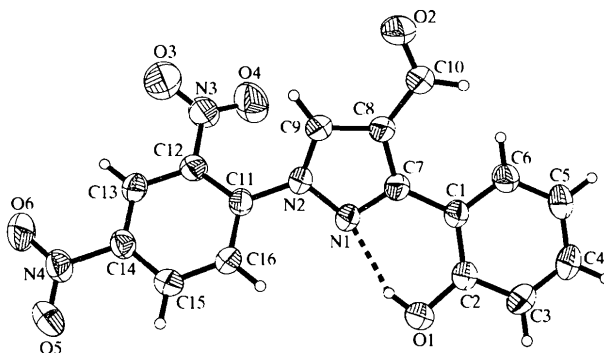


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The nitro group in the *o*- position is tilted 22.1 (2)° to the plane of the phenyl ring, whereas the nitro group in the *para* position is almost coplanar [dihedral angle 3.5 (1)°] with the phenyl ring. This phenomenon may be related to the electron-withdrawing character of the nitro group. Whilst the dinitrophenyl and hydroxyphenyl groups are twisted through 43.8 (1) and 28.0 (1)°, respectively, with the pyrazole ring, they make a dihedral angle of 20.9 (1)° with each other. The six-membered ring formed by the intramolecular hydrogen bond between the hydroxy group and the N1 atom of the pyrazole ring is twisted through 9.7 (1) and 24.0 (1)° with the phenyl and pyrazole rings.

Apart from normal van der Waals interactions, the molecular structure is stabilized by an intramolecular O—H...N hydrogen bond involving the pyrazole ring and carbaldehyde group. The nitro groups are involved

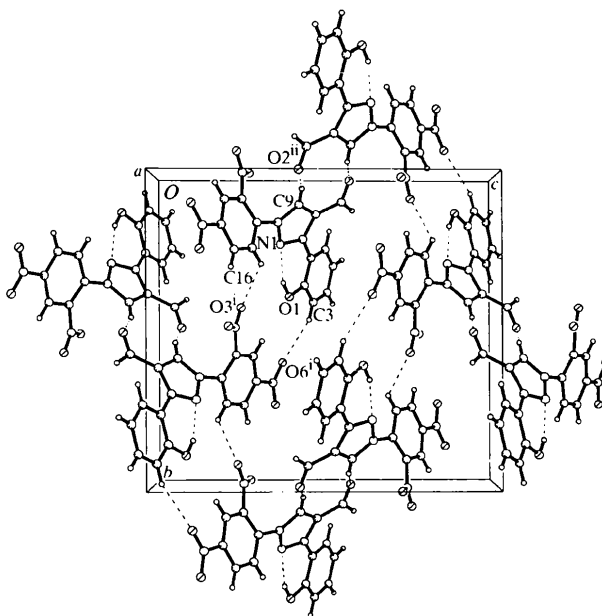


Fig. 2. Packing of molecules viewed down the *a* axis.

in a three-dimensional network of C—H...O hydrogen bonds (Fig. 2) which stabilizes the molecular packing in the solid state (Table 2).

Experimental

o-Hydroxyacetophenone-2,4-dinitrophenylhydrazone (1.58 g, 0.005 mol) was dissolved in *N,N*-dimethylformamide (5 ml) and kept ice cold. To this, POCl₃ (1.4 ml) was added dropwise with stirring for 15 min. After 3–4 h stirring at room temperature, the reaction mixture was poured onto 100 g of crushed ice. The yellow precipitate obtained was filtered, washed and dried. The product was purified using column chromatography with silica gel (60–120 mesh) and 20% ethyl acetate–petroleum ether as eluent. Finally, the title compound was obtained (yield 1.52 g) and recrystallized from ethyl acetate by slow evaporation.

Crystal data

C₁₆H₁₀N₄O₆
M_r = 354.28
 Monoclinic
*P*2₁/*c*
a = 6.3799 (1) Å
b = 14.9302 (2) Å
c = 16.1080 (2) Å
 β = 91.636 (1)°
V = 1533.71 (4) Å³
Z = 4
D_x = 1.534 Mg m⁻³
D_m not measured

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 12 024 measured reflections
 3751 independent reflections

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.055
wR(*F*²) = 0.155
S = 1.027
 3751 reflections
 235 parameters
 H atoms constrained
w = 1/[$\sigma^2(F_o^2) + (0.0708P)^2 + 0.5383P$]
 where *P* = (*F_o*² + 2*F_c*²)/3

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 8102 reflections
 θ = 1.86–28.34°
 μ = 0.121 mm⁻¹
T = 293 (2) K
 Block
 0.48 × 0.32 × 0.28 mm
 Orange

2750 reflections with
 $I > 2\sigma(I)$
*R*_{int} = 0.056
 θ_{\max} = 28.57°
h = -8 → 4
k = -19 → 18
l = -19 → 21

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max}$ = 0.471 e Å⁻³
 $\Delta\rho_{\min}$ = -0.272 e Å⁻³
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O3—N3	1.208 (3)	N1—N2	1.372 (2)
O4—N3	1.212 (3)	N2—C9	1.344 (2)
O5—N4	1.219 (2)	N2—C11	1.433 (2)
O6—N4	1.212 (2)	N3—C12	1.479 (3)
N1—C7	1.343 (2)	N4—C14	1.484 (2)
C7—N1—N2	105.7 (1)	C9—C8—C7	104.7 (2)
C9—N2—N1	111.2 (1)	C9—C8—C10	123.5 (2)

C9—N2—C11	127.8 (2)	C7—C8—C10	131.6 (2)
N1—N2—C11	120.2 (1)	O2—C10—C8	122.1 (2)
N1—C7—C8	110.2 (2)	C13—C12—C11	121.6 (2)
N1—C7—C1	120.4 (2)	C13—C14—C15	122.3 (2)
C8—C7—C1	129.4 (2)		

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1A...N1	0.84	1.93	2.718 (2)	155
C3—H3A...O6'	0.93	2.57	3.455 (3)	159
C9—H9A...O2''	0.93	2.39	3.163 (3)	140
C10—H10A...O5'''	0.93	2.59	3.075 (3)	113
C16—H16A...O3'	0.93	2.56	3.264 (3)	132

Symmetry codes: (i) 1 - *x*, $\frac{1}{2}$ + *y*, $\frac{1}{2}$ - *z*; (ii) 1 - *x*, -*y*, 1 - *z*; (iii) *x* - 1, $\frac{1}{2}$ - *y*, $\frac{1}{2}$ + *z*.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1310). Services for accessing these data are described at the back of the journal.

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